Name: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Block: \_\_\_\_ Date: \_\_\_\_\_\_\_

**Thermochemistry**

(We’ll follow different resources for the unit. The main resource is Kotz & Treichel, Chemistry & Chemical Reactivity, 2003, Chapter 6, pages 200-249)

1. Energy

* Definition and classification
* Law of Conservation of energy
* Temperature
* Heat Transfer & thermal equilibrium – exothermic versus endothermic
* Specific Heat and heat capacity
* Change of State – Heating Curves

1. First Law of Thermodynamics

* Definition of internal energy, heat and work
* Exothermic versus endothermic reactions

1. Enthalpy- definition

* Enthalpy of formation
* Enthalpy of a reaction
* Hess’ Law- separate lecture-Calorimeter Lab activity

1. Calorimetry –

At constant pressure calorimeter experiments- Heat of solution

Constant volume calorimeter experiments

* Hess’ Law-Calorimeter Lab activity

1. **Energy**

***Energy*** (E or U) - is the capacity to do work (W) or to produce heat (Q). Energy is a ***state function***, does not depend on a pathway, it depends only on the present state.

**Work i**s defined as force acting over a distance.

***Heat*** is the energy that flows between objects that become in contact if they are at different temperatures. It is an extensive property of matter, depends on the amount of matter.

Work and heat depend on specific conditions, or pathway, not so energy.

ΔE = Q + W

Internal Energy = Heat + work

**Energy Units**

|  |  |  |
| --- | --- | --- |
| Name | Unit | Symbol |
| 1 Joule | 1 | J |
| 1 kilojoule | 1000 Joules | kJ |
| 1 calorie | 4.184 Joules | cal |
| 1 Calorie (“food calorie) | 1000 calories =4184 Joules | Cal |

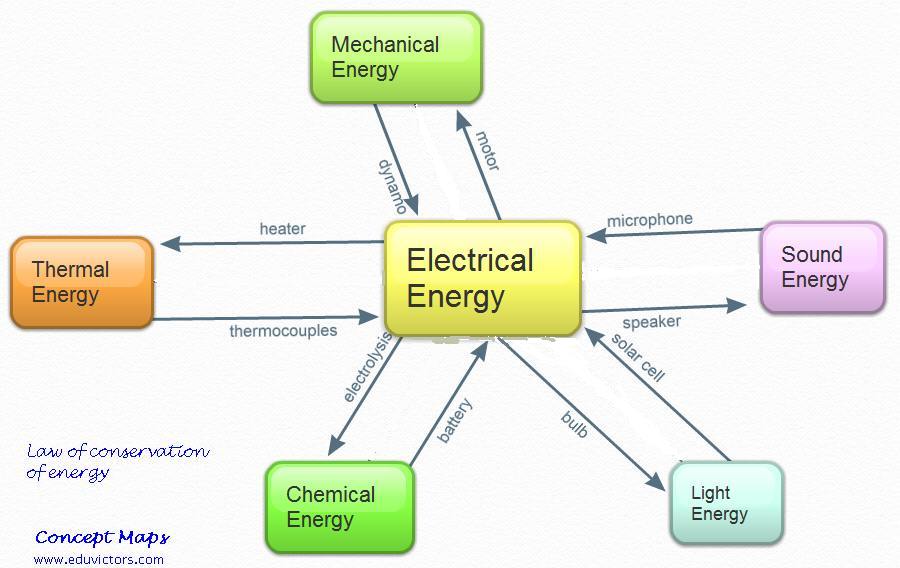
***Classification of Energy***

Potential energy- is the energy due to position or composition. Example: chemical, electrostatic energy, gravitational.

Kinetic energy – is the energy due to motion of the object and depends on the mass of the object, m, and its velocity, v: KE = mv2

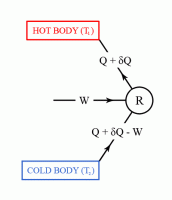
Examples: thermal, mechanical, electrical, light, sound.

First Law of Thermodynamics or Law of Conservation of energy- states that energy can be converted from one form to another but can be neither created nor destroyed.



***Second law of Thermodynamics***

The second law of thermodynamics states that heat cannot be transferred from a body at a lower temperature to a body at a higher temperature without the application of energy from an external source.

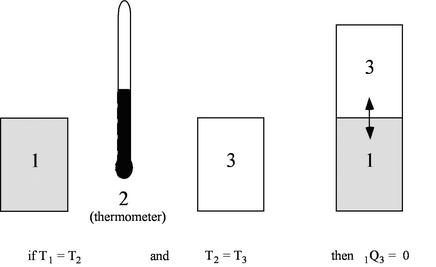


***Third law of Thermodynamics***

The **third law** states that the **entropy** of a pure crystal at absolute zero is zero. Since there can be no physical system with lower entropy, all entropy is thus defined to have a positive value.(entropy is the degree of disorder of particles in a system)

Zeroth Law: There exists for every thermodynamic system in equilibrium a property called temperature. Equality of temperature is a necessary and sufficient condition for thermal equilibrium.

The Zeroth Law thus defines a property (temperature) and describes its behavior



***No heat is transfer when systems in contact are at the same temperature***

***Temperature*** is the property that describes the random motion of the particles of a specific substance in terms of their kinetic energy; it is an average. It is also an intensive property of matter, depends on the kind of substance, not on its amount. It is defined by the Zeroth Law of Thermodynamics.

***Heat Transfer Process***

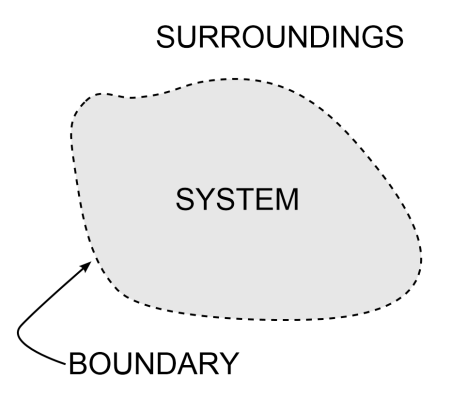
To define heat transfer, system and surroundings must be define first. ***System*** is a part of the universe that is under study, ***surrounding*** is the rest of the universe; boundary is what separates both of these.

Heat is transferred between system and surroundings

System ← Heat →Surroundings

Endothermic

Heat

 Heat

Exothermic

Heat transfer occurs when two objects at a different temperature come in contact. The flow of heat will continue until both objects reach the same temperature, this is known as ***“thermal equilibrium”.***

Two types of heat flow can be defined:

***Endothermic*** Process: Heat flows from the surroundings to the system, Q > 0

***Exothermic*** process: Heat flows from the system to the surroundings, Q < 0

***Specific Heat Capacity (c or s)***

It is the amount of heat required to raise the temperature of 1 g of a substance by 1 kelvin.

It is an intensive property of matter, depends only on the type of substance not on its amount.

Specific heat capacity equation

c =

Q = heat when no change of state occurs.

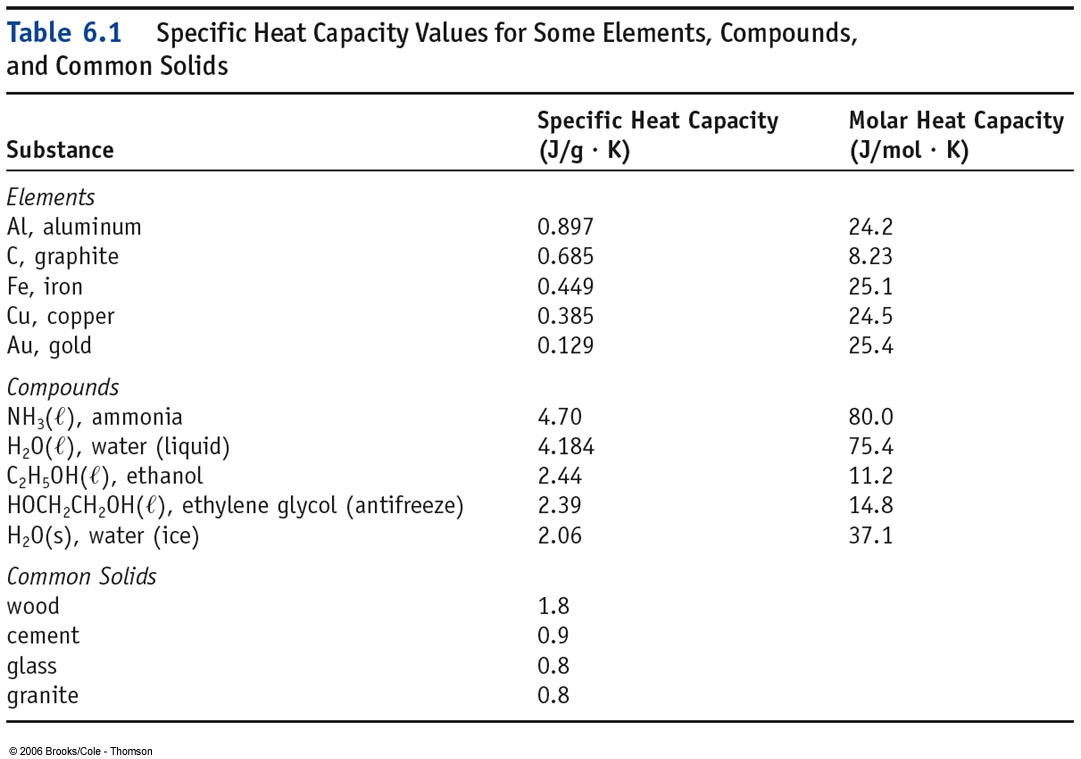
m = mass in grams

c = specific heat capacity

ΔT = Tf – Ti, in Celsius or Kelvin degrees.

Conversion Factors

|  |  |
| --- | --- |
| Unit | Conversion factor |
| Q (heat) | 1 cal =4.184 J |
| 1 kilojoules | 1kJ = 1000 J |
| T (temperature) | K = 0C + 273 |



Kotz & Treichel, *Chemistry & Chemical Reactivity*, 2003, p. 210

***Heat Capacity (C)*** It is equal to the amount of heat needed to increase the temperature of an object exactly one degree Celsius (or Kelvin). It depends on both its mass and its chemical composition. It is an extensive property of matter because it depends on the amount of substance. It also depends on the specific heat capacity of the substance.

Heat Capacity Equation

C = =m x c

Example- A piece of silver has a heat capacity of 42.8 J/0C and a mass of 182 g. Calculate the specific heat of silver.

Specific heat capacity = Heat capacity/ mass c = c = = 0.235 J/oC.g

Example- When 435 J of heat is added to 3.4 g of olive oil at 21 0C, the temperature increases to 850C. What is the specific heat of olive oil?

c = c = = 1.99 J/g.0C

Example- Calculate the amount of heat necessary to raise the temperature of 1235 g of water, from 25 0C to 65 0C. The specific heat capacity of water is 4.184 J/g.K

The difference of temperature in Kelvin or Celsius degrees is numerically the same

(85 + 273)K –(25+273)K = (85-25) = 60 K

Q = m.c.ΔT

Q = (1235 g) x (4.184 J/g.K) x 60 K = 310034.4 J

If given in kilojoules: Q = 310034.4 J x = 310 kJ

**Homework # 1 – p. 241-242 Review Concepts 1,3 & 5 and Practicing skills: 12-25 (odd only)**

***Energy and Changes of State***

**Heating Curves**

Let's examine the heat and enthalpy changes for a system undergoing physical change.

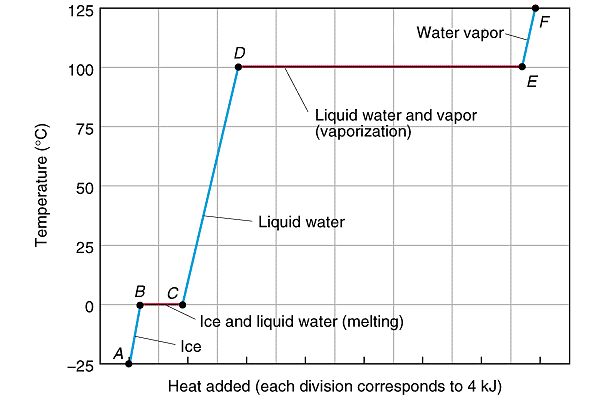
A good example that most people are familiar with is the heating of water. If we take a beaker filled with ice (solid water) and put in on a hot plate that has a temperature of 125 ° C. We all know what will happen. First the ice will melt to liquid water. Then the water will increase in temperature. Then finally the water will boil. During this entire process the temperature of the hot plate will be higher than the temperature of the beaker of water. Thus, during this entire process energy will flow in the form of heat from the hot plate into the water. We would likely describe the water as the system and the hot plate as a constant temperature surrounding.

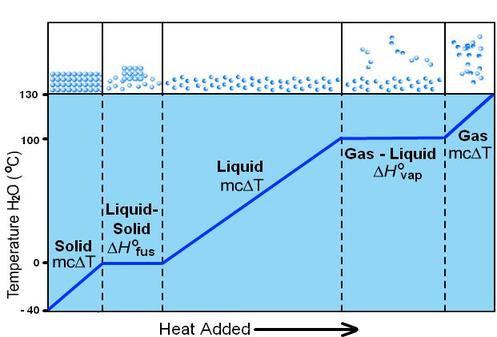
For this process we are interested in the amount of heat that flows from surroundings into the system. Remember, heat can be tricky. When there is no chemical change or phase change, then energy flowing into a system in the form of heat will lead to a temperature change only. However, when there is chemical change or a phase change, then energy will flow in to make these changes possible and the temperature will stay constant. Why doesn't the temperature go up? The energy coming in results in higher potential energy not higher kinetic energy. Breaking up the intermolecular forces between the molecules leads to a high potential energy. Intermolecular forces are what determine a physical state of the matter, the strongest are present in the solid state, the weakest one, or practically none existent, in the gaseous state.

This can be easily seen in a heating curve that plots the temperature of a system as a function of the heat flow into the system. Initially the system is a solid, then it has a melting transition, then it is a liquid, and then has a vaporization transition, and then it is a gas.

The diagram below shows the heating curve for water. The temperature of the system is plotted as function of time. Heat is flowing at a constant rate. (Constant rate flow is an approximation)

The heating of a sample of water from -25 to 125 oC involves both the heat capacities of the pure phases but also the enthalpies of the melting (fusion) and boiling (vaporization) of the water.



<http://www.chem.ufl.edu/~itl/2045/lectures/lec_f.html>

<http://www.dlt.ncssm.edu/TIGER/Flash/phase/HeatingCurve.html>

Calculations for a Heating Curve Process – Calculating the total amount of heat absorb

There are two types of calculations on the curve, one where there is no change of phase, only a change of temperature and another where there is a change of phase at a constant temperature. The amount of heat absorb by the system, is equal to the sum of the heat absorbed in each step.

For 50 g of ice are heated from – 25 0C to 125 0C, the following steps occur:

Step 1: No change of phase H2O(s, -25 0C) 🡪 H2O (s, 0 0C) q1 = m. c ice. ΔT

Step 2***: Change of phase*** **H2O (s, 0 0C) 🡪 H2O (l, 0 0C) q2 = H fuss . m**

Step 3: No change of phase H2O (l, 0 0C) 🡪 H2O(l, 100 0C) q3 = m.c water.

Step 4: ***Change of phase* H2O (l, 100 0C) 🡪 H2O (g, 100 0C) q4 = H vap . m**

Step 5: No change of phase H2O (g, 100 0C) 🡪 H2O(g, 125 0C) q 5 = m.c vapor.ΔT

|  |  |  |
| --- | --- | --- |
|  | Specific Heat J/g.K | Enthalpy of Phase change |
| H2O (s), Ice | 2.06 J/g.K | Solid 🡪 liquid: H fussion = 333 J/g |
| H2O (l), Liquid water | 4.184 J/g.K |  |
| H2O (g), Steam | 2.03 J/g.K | Liquid 🡪 gas: H vap = 2256 J/g |

q1 = 50g. 2.06 J/gK. (0 –(-25)) K = + 2575 J

q2 =333 J/g . 50 g = +16650 J

q 3 =50g .4.184 j/g.K . (100-0) K = +20920 J

q 4 = 2256 J/g . 50 g = +112800 J

q 5 = 50 g . 2.03 J/g.K . (125 -100) K = +2537.5 J

Total Heat Q = q1 + q2 + q3 + q4 + q5 = 155482.5 J , in kilojoules Q = 155.5 kJ

**Homework # 2: p.242 #26-33 (all)**

***2. First Law of Thermodynamics***

“The energy of the universe is constant”, consequently, the first law of thermodynamics states that for any discrete system, the amount of energy coming into the system, is equal to the amount of energy getting out of the system. Internal energy is in turn the amount of heat added to the system and the amount of work done by the system.

From the system point of view (changes are”measured” in the system)

**ΔE = Q + W**

**Internal energy = amount of heat change + amount of work change**

The amount of heat change can be positive (endothermic process) or negative (exothermic process)

The amount of work change in the system can be positive, +W, if work is done on the system by the surroundings, or negative, -W, if the work is done by the system into the surroundings.

*Note: In engineering the first law of thermodynamics, work is observed from the surroundings point of view, so the first law of thermodynamics equation looks like this:*

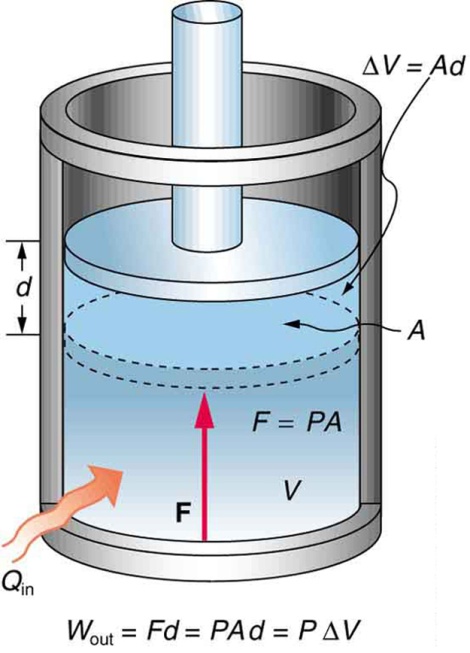
*ΔU = Q – W*

*Internal energy = heat added to the system – work done by the system into the surroundings*

**Understanding Work through an experiment:** Gas expanding in a sealed container with a mobile piston (no friction exist between the piston and the walls of the container)

A process by which a gas does work on a piston at constant pressure is called an isobaric process.

Δh V = A Δh



***W out = F Δh = PA Δh = PΔV***

An isobaric expansion of a gas requires heat transfer to keep the pressure constant.

The picture shows an expanding gas exerting pressure P over the piston of area A. By doing so is capable of moving the piston a distance d, or more like a height “h”. The change in height is equal to Δh (Δh is read “delta h” means the difference of height from beginning to end of the process, Δh = hf – hi)

Pressure is defined as force per unit area, the pressure of the gas is:

P =

Work is the defined as the force applied over a distance, in this case the distance is equal to Δh W = F Δh

W = F x Δh, replacing F as F = PxA

W = (PxA) xΔh , regrouping A and Δh

W = P x (AxΔh), Area and height becomes volume,

**W = P x (ΔV**) or W = P (Vf – Vi)

Example (Adapted from Zumdahl, Chemistry, 2012) - A balloon is being inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from 400 L to 450 L by the addition of 1.3 x 10 4J or 13 kJ of energy as heat. Assuming that the balloon expands against a constant pressure of 1.0 atmospheres, calculate the resulting internal energy, ΔE, for the process. Unit conversion needed, 1 L. atm = 101.3 J

Data

Vi = 400 L

Vf = 450 L

Q = 1.3 x 10 4 J

P = 1.0 atm

Equation for internal energy is: ΔE = Q + W

Solution

Q is given, so calculate work

W = P ΔV = P(Vf –Vi)

W = 1.0 atm ( 450-400) L = 1.0x 50 atm.L=

W = 50.0 atm.L x = 5065 J

The work is done on the surroundings therefore W is negative, -5065 J

Now we have everything we need

Q = 1.3 x 104 J and W = - 5065 J

ΔE = Q + W

ΔE = 1.3x104 J -5065 J =+7935 J

Since there is more heat given to the system than the work done by it, there is a net increase on the internal energy of the balloon, hence ΔE is positive.

1. **Enthalpy (H)**

Is defined as: H = E + PV

E = internal energy of the system

P = pressure of the system

V = volume of the system

In a process carried out at constant pressure where work is done by the system (w =-PΔV)

ΔE = Qp + W 🡪 ΔE = Qp - PΔV

***Qp = ΔE + PΔV***

The enthalpy change is: ΔH = E + Δ(PV)

At constant pressure: ***ΔH = ΔE + PΔV***

Therefore, ***ΔH = Qp***

Enthalpy change is equal to heat change at constant pressure.

ΔH is read “delta H” , for a chemical reaction ΔH is equal to:

ΔH = H products – H reactants

Qp is heat at constant pressure

Characteristics of ΔH

1. The ΔH of formation of pure elements in their standard state is zero., ΔH0f (C ,s) = 0

|  |
| --- |
| Conventional Definitions of Standard States  Zumdhal, Chemistry 2012 |
| For a compound   * The standard state of a gaseous substance is a pressure of exactly 1 atmosphere. * For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid. * For a substance present in a solution, the standard state is a concentration of 1 mol/L or 1 M   For an Element   * The standard state of an element is the form in which the element exists under conditions of 1 atmosphere and 25 0C. (The standard state of oxygen is O2 (g) at a pressure of 1 atmosphere, the standard state of sodium is Na(s); the standard state of mercury is Hg (l); and so on. |

1. The ΔH of a reaction is equal to the difference between the sum of the enthalpy of formation of all products minus the sum of the enthalpy of formation of all products.

ΔH reaction = ΣH0 f (Products) – ΣH0f (reactants)

*Note: the symbol “Σ” means sum, it is the capital letter “S” in Greek.*

1. If a reaction is reversed, its ΔH sign changes to its opposite.
2. If a compound has a coefficient in the equation, its ΔH 0f is multiplied by the same number.

Example 1: What is the enthalpy of formation for water liquid at 25 0C?

H2 (g) + O2 (g) 🡪 H2O (l)

ΔH rxn = ΣΔH f prod – ΣΔH f react

ΔH rxn = 1 mol .ΔH 0f (H2O,l) – [ mol. ΔH0f(H2,g) + 1 mol. ΔH0f(O2,g) ]

From tables ( Kotz & Treichel, Chemistry & Chemical Reactivity, 2003, Appendix LTable 20 page A33)

ΔH rxn = 1 mol. -286 kJ/mol – [ mol. 0 kJ/mol + 1 mol. 0 kJ/mol]

ΔH rxn = -286 kJ

Example 2- What is the enthalpy for the decomposition of water into its elements?

H2O(l) 🡪 H2(g) + O2 (g)

If the enthalpy of Formation of water releases -286 kJ, in an exothermic process, the enthalpy of decomposition absorbs + 286 kJ, meaning that it is an endothermic process.

***Hess’ Law***

Since enthalpy is a state function, independent of the pathway, in a chemical process, the enthalpy of a reaction is the same whether the process has one or multiple steps.

Example: (Kotz & Treichel, Chemistry & Chemical Reactivity, 2003, p.226)

What is the enthalpy for the reaction below?

C(s) + O2(g) 🡪 CO (g) ΔH = ?

Data

CO (g) + O2 (g) 🡪 CO2 (g) ΔH = -283.0 kJ

C(s) + O2(g) 🡪 CO2(g) ΔH = -393.5 kJ

* Use both reaction for which the ΔH is known.
* Reverse the first reaction to have CO (g) in the product side, change the sign for its ΔH

CO2 (g) 🡪 CO (g) + O2(g) ΔH = + 283.0 kJ

* Leave the second reaction as is, since it will allow to cancel out the CO2 and ½ of the O2
* “Add” both reaction together, add their ΔH together as well

CO2 (g) 🡪 CO (g) + O2(g) ΔH = + 283.0 kJ

C(s) + O2(g) 🡪 CO2(g) ΔH = -393.5 kJ

C(s) + O2 (g) 🡪 CO (g) ΔH = +283.0 -393.0 = ***-110.5 kJ***

**Homework # 3:**

Enthalpy p.243 # 34-37 odd only

Hess’ Law p. 244 # 50-53 all

Standard Enthalpies of Formation p. 244-245 # 54-65 odd only.

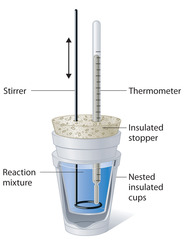
1. ***Calorimetry***

It is an experimental technique that measures the heat transferred in a chemical of physical process. It uses a calorimeter. There are two types of calorimetry experiments.

Constant Pressure Calorimetry

In a constant pressure calorimeter experiment, the system’s immediate surrounding is water. The heat change is measured in the immediate surroundings.

A constant pressure calorimeter consists on an insulated container that isolates the immediate surroundings from the rest of the universe. The system is either a chemical reaction or a solid that does not chemically interact with water. . The calorimeter is fitted with a thermometer and a stirrer to allow for a uniform distribution of heat.



The insulation allows to assume that all the heat exchanged is between the system and its immediate surroundings, like this

q sys + q H2O = 0

where q = m.c.ΔT

It is possible to calculate the specific heat capacity of unknown solids, or the heat of reactions in aqueous solutions.

Example- What is the heat capacity of an alloy if 25 g at 100 0C is placed in a constant pressure calorimeter containing 250 g of distilled water at 25 0C. The final temperature was 34 0C. The specific heat capacity of water is 4.184 J/g.K

Data

|  |  |  |
| --- | --- | --- |
|  | Alloy | H2O |
| Mass | 25 g | 250g |
| Specific heat capacity | c | 4.184 J/g.K |
| Initial temperature | 100 0C | 25 0C |
| Final temperature | 34 0C | 34 0C |

Note: the final temperature is the same for both. It is the temperature at which thermal equilibrium occurs, and no more heat flows.

q alloy + q H2O = 0

q alloy = 25 g.C. (37-100) K = -3150g.K . c , the metal looses heat to the water.

q H2O = 250 g x 4.184 j/g.K . (34-25) K = +9414 J , water gained heat from the alloy

-3150 g.K. c + 9414 J = 0

315 c g.K = 9414 J

c = = 2.988 J/g.K

Example- In a constant pressure calorimeter experiment, what will the final temperature be if 45 g of copper at 100 0C where placed in 250 g of distilled water at 25 0C?

Specific heat capacity of copper is 0.385 J/g.K and for water is 4.184 J/g.K

|  |  |  |
| --- | --- | --- |
|  | copper | water |
| Mass | 45 g | 250 g |
| Specific heat capacity | 0.385 J/g.K | 4.184 J/g.K |
| Initial temperature | 100 0C | 25 0C |
| Final temperature | Tf | Tf |

q cu + q H2O = 0

45 g .0.385 J/g.K (Tf – 100) K + 250 g. 4.184 J/g.K x (Tf – 25) K = 0

17.325 (Tf – 100) + 209.2 (Tf – 25) = 0

17.325 Tf -1732.5 + 209.2 Tf -5230 = 0

Tf (17.325+209.2) -1732.5-5230 = 0

Tf (226.525) -6962.5 = 0

Tf (226.525) = 6962.5

Tf = = 30.73 0C

Example – Heat of reaction in aqueous solution. When 70 mL of water containing 0.1 00 mol HCl at 21.0 0C is added to 75 mL of water containing 0.100 mol NaOH at 21.0 0C in a constant pressure calorimeter, the temperature of the solution increases to 29.6 0C. Calculate the enthalpy change in kJ during this reaction.

Data

|  |  |  |
| --- | --- | --- |
|  | HCl | NaOH |
| amount | 0.1 mol | 0.1 mol |
| volume | 75.0 mL | 75.0 mL |
| Initial temperature | 21.00C | 21.0 0C |
| Final temperature | 29.6 0C | 29.6 0C |

Solution

The reaction occurs at the molecular level between HCl and NaOH. The heat changes will be measured in the solvent, water.

Total Volume = 75 mL + 75 mL = 150 mL of water

Assume the solutions have density 1.00 g/mL

Mass of water = 150 mL x 1.00 g/mL = 150.0 g water

Specific heat capacity of the solution = 4.184 J/g.K, we assume the solutions have the same specific heat capacity as water alone.

Change in temperature + (29.6 – 21.0 )K = 8.6 K

The heat absorbed by the water is the heat released by the reaction, In a constant pressure calorimeter,

q H2O + q rxn = 0

q H2O = 150 g . 4.184 J/g.K x 8.96 K = 5397.86 J

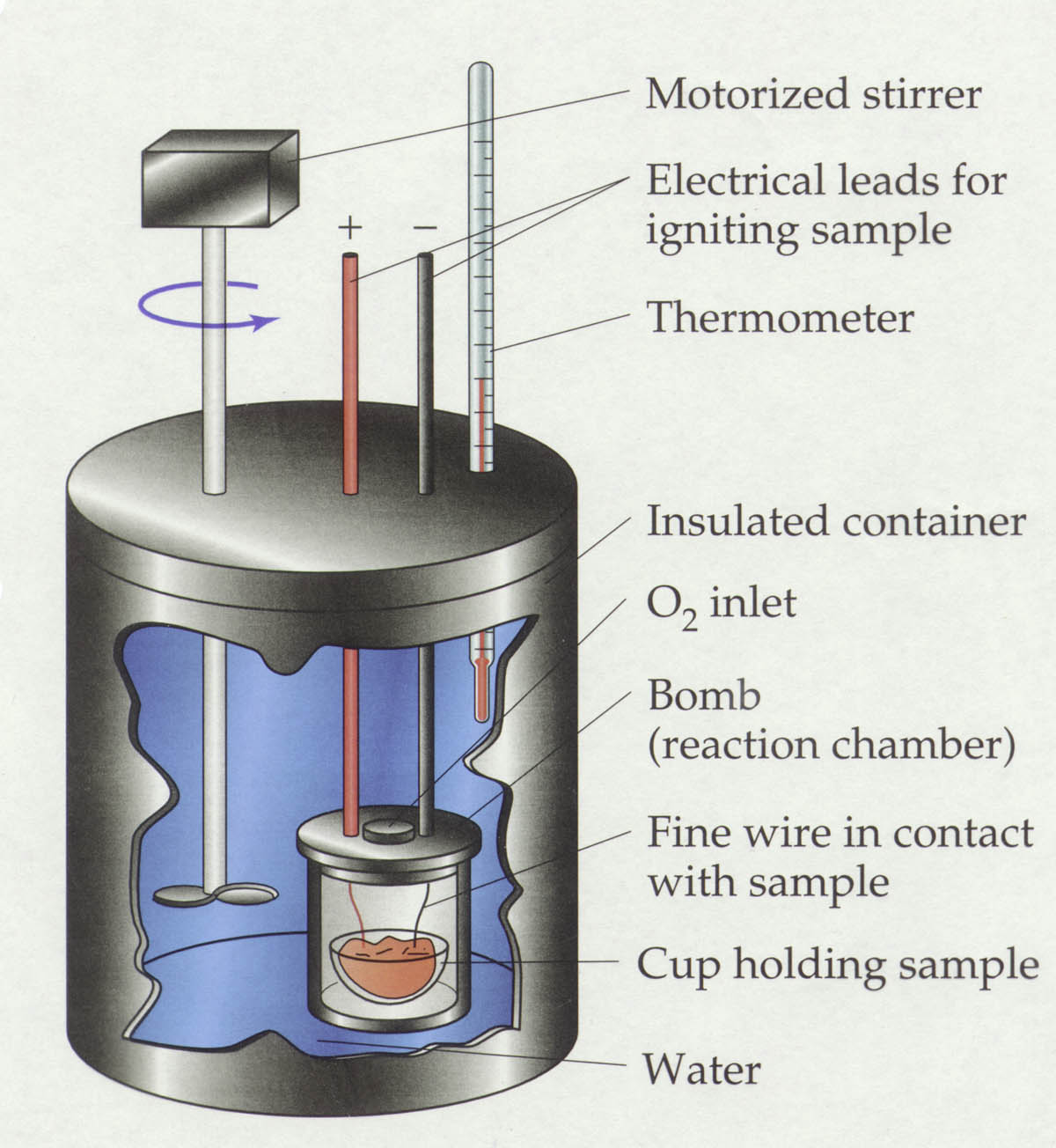
5397.86 J + q rxn = 0

q rxn = - 5397.86 J

Constant Volume Calorimeter

It is a method used to measure the heat of combustion reactions, or the caloric value of foods.

In a constant volume calorimeter the heat produced in a reaction is equal to the internal energy, there is no work done by the gases produced because the volume is kept constant. The heat is absorbed by the calorimeter itself and by the water surrounding the calorimeter. Water is again the immediate surroundings where all measurements of heat change will be measured by measuring the change in temperature.



q rxn + q bomb + q H2O = 0

Example- A 1.00 g simple of sugar is burned in a constant volume calorimeter, or bomb calorimeter. The temperature of 1.50 x 10 3 g of water in the calorimeter rises from 25.00 0C to 27.32 0C. The heat capacity of the bomb is 837 J/K and the specific heat capacity of the water is 4.184 J/g.K. Calculate the heat evolved per gram.

Data

Mass of sample = 1.0 g (C12 H22 O11)

Mass of water = 1.50 x 10 3 g

Initial Temperature of water = 25 0C

Final temperature of water = 27.32 0C

Heat capacity of the Bomb = 837 J/K

Calculations

q rxn + q bomb + q H2O = 0

q rxn= ?

q bomb = C bomb x ΔT

q H2O = m.c.ΔT

q bomb = 837 j/K (27.32 – 25.00) K = 1841.2 J

q H2O = 1.50 x 10 3 g x 4.184 J/g.K (27.2 – 25) K = 13807.2 J

q rxn + 1841.1 J + 13807.2 J = 0

q rxn = -1841.2 J -13807.2 J = -15648.4 J or 15.648 kJ

**Homework # 4 : p.243 # 38-49 odd only.**